

Estuarine Colloids: Sorption Capacity, Colloid Facilitated Transport and Bioavailability

Principal Investigators:

Dr. Peter H. Santschi, Professor, Dept. of Oceanography, Texas A&M University, Galveston, TX
77553-1675
Phone: 409-740-4476; Fax: 409-740-4786;
E-Mail: santschi@tamug.tamu.edu

Dr. Gary A. Gill, Assoc. Professor, Dept. of Oceanography, Texas A&M University, Galveston, TX
77553-1675
Phone: 409-740-4710; Fax: 409-740-4786;
E-Mail: gillg@tamug.tamu.edu

Dr. Mark Benfield, Research Scientist, Louisiana State University, Baton Rouge, LA
Phone: 504-388-6372; Fax: 504-388-6513
E-Mail: benfie@unix1.sncc.lsu.edu

Award # N00014-93-1-0877, Modification No. P00006

LONG-TERM GOALS

To gain a better understanding of the role of colloidal organic macromolecules and inorganic colloidal microparticles in the cycling, speciation and bioavailability of trace elements in coastal waters.

SCIENTIFIC OBJECTIVES

1. Continue to critically evaluate ultra-filtration methodology for the collection of colloidal matter from fresh, estuarine and sea water.
2. Investigate changes in the phase distribution of selected trace metals and metalloids in estuarine water along salinity transects.
3. Determine the importance of coagulation of colloidally bound trace metals (e.g., Ag, Hg, Se, As, Sb, Cd, Cu, Co, Ni, Pb, Zn, Fe) in estuarine waters.
4. Determine the bioavailability of colloidally bound trace elements and metalloids to penaeid shrimp.
5. Develop new analytical methods to establish binding of trace elements (e.g., Ag) with natural organic macromolecules and colloidal organic matter in the estuarine environment.
6. Evaluate microscopy imaging approaches to determine forms, shapes and sizes of natural organic macromolecules and inorganic microparticles (i.e., colloids).

APPROACH

- 1) **Colloid collection methodology:** Test the optimal concentration factor for cross flow ultrafiltration (CFUF) for preconcentration and isolation of colloidal organic matter (COM) from 1 - 100 L of river, estuarine and sea water samples.

| Report Documentation Page | | | Form Approved OMB No. 0704-0188 | | |
|--|------------------------------------|-------------------------------------|---|---|---------------------------------|
| Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. | | | | | |
| 1. REPORT DATE 1998 | | 2. REPORT TYPE | | 3. DATES COVERED 00-00-1998 to 00-00-1998 | |
| 4. TITLE AND SUBTITLE Estuarine Colloids: Sorption Capacity, Colloid Facilitated Transport and Bioavailability | | | | 5a. CONTRACT NUMBER | |
| | | | | 5b. GRANT NUMBER | |
| | | | | 5c. PROGRAM ELEMENT NUMBER | |
| 6. AUTHOR(S) | | | | 5d. PROJECT NUMBER | |
| | | | | 5e. TASK NUMBER | |
| | | | | 5f. WORK UNIT NUMBER | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Texas A&M University ,Department of Oceanography,Galveston,TX,77553-1675 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | | | | 10. SPONSOR/MONITOR'S ACRONYM(S) | |
| | | | | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) | |
| 12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited | | | | | |
| 13. SUPPLEMENTARY NOTES See also ADM002252. | | | | | |
| 14. ABSTRACT | | | | | |
| 15. SUBJECT TERMS | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT Same as Report (SAR) | 18. NUMBER OF PAGES 5 | 19a. NAME OF RESPONSIBLE PERSON |
| a. REPORT unclassified | b. ABSTRACT unclassified | c. THIS PAGE unclassified | | | |

- 2) **Colloidal trace element distribution:** Conduct salinity transects of the phase speciation distribution of trace metals, metalloids and organic carbon isotopes in Galveston Bay.
- 3) **Coagulation rates of colloiddally bound trace metals:** Conduct radiotracer experiments using colloids isolated through CFUF and dialysis to investigate coagulation rates of colloiddally bound trace metals to colloids and suspended particles (\bullet 0.4 μ m).
- 4) **Bioavailability of Colloiddally Bound Trace Metals to Penaeid Shrimp:** Evaluate experimental results on uptake and depuration using penaeid shrimp, exposed to radioactive trace metals in colloidal or free-ionic forms.
- 5) **Binding of selected trace metals to organic macromolecules:** Evaluate HPLC separation with thiol detection after addition of Ag and fluorescent tag to colloids.
- 6) **Forms, sizes and shapes of colloids:** Evaluate results from Atomic Force Microscopy (AFM) and Transmission Electrom Microscopy (TEM) of natural colloids in collaboration with Drs. Jacques Buffle and Kevin Wilkinson, University of Geneva, Switzerland.

WORK COMPLETED

Objective 1 has been completed, as far as the CFUF methodology for the collection and analysis of bulk organic carbon and a number of trace metals is concerned.

Objective 2 has been completed, and results are described in several publications. Reviews of the subject have also been presented at a number of national and international meetings.

Objective 3 has been completed and published.

Objective 4. Experimental work has been completed, and initial results are described in a master thesis (R. Carvalho, 1996) and in a manuscript which is in review.

Objective 5 has been initiated, and preliminary results have been described at national meetings.

Objective 6 has been completed, and results are published.

RESULTS

- 1) We showed in separate laboratory experiments that it is best to use high concentration factors when the purpose is to collect a high molecular weight fraction of organic matter for the determination of trace constituents. This is due to the sensitivity of low molecular weight molecules to entrainment into the high molecular weight fraction (Guo and Santschi, 1998) during cross flow ultrafiltration.
- 2) The trace metal composition of the freeze-dried and diafiltered colloidal (1kDa to 0.4 μ m) fraction of natural organic matter in Galveston Bay, Gulf of Mexico and Middle Atlantic Bight waters clearly showed an enrichment pattern similar to the Irving-Williams Series for the different trace metals, when normalized to organic carbon or Al concentrations (Guo and Santschi, 1998, in review). Ratios of colloidal metal (e.g., Ag, Cu and Hg) to 0.4 μ m filter-passing metal correlated with the ratios of COC to total DOC, suggesting that functional groups with high affinity for these metals were relatively evenly distributed over the different molecular weight fractions (Wen et al., 1998).
- 3) When COM was labeled with various trace metals in radioactive form, coagulation with natural suspended matter occurred over the course of hours, while slower uptake was observed over the course of days. Results, which indicated that colloids can serve as intermediaries in the transfer and removal of trace metals in estuarine systems, could be explained by postulating two major groups of surface active trace metal complexants: A major component (e.g., a biopolymer) which coagulates

at a constant rate, but complexes trace metals to different extents, and a minor complexant (e.g., a phytochelatin), which complexes and coagulates different trace metals at different rates (Wen et al., 1997).

- 4) Radiotracer experiments to compare bioaccumulation and bioavailability to penaeid shrimp, sites of accumulation and depuration of trace metals in colloiddally complexed and free-ionic forms demonstrated that colloiddally bound metals are bioavailable to shrimp. Differences were noted in the rates and extent of uptake and depuration between the colloiddal and free-ionic treatments for whole body and individual tissues. Depuration of metals was noted for both treatment regimes, with metals introduced as free ionic species showing greater retention in shrimp than metals introduced as colloiddally bound species. Results were consistent with the hypothesis that colloiddally bound metals entered the body through the gills (Carvalho et al., 1998).
- 5) Preliminary evidence suggests that silver in Galveston Bay colloids is complexed to sulfhydryl groups (Santschi et al., 1997).
- 6) Colloiddal organic matter, isolated by cross-flow ultrafiltration, was imaged by a new technique, Atomic Force Microscopy, and compared to Transmission Electron Microscopy. Preliminary results suggest that polysaccharide rich fibrils of recent origin (with younger radiocarbon age) are a major component of COM (Santschi et al., 1998).

IMPACTS

Proper adaptation of CFUF using clean techniques make it not only suitable for isolating organic carbon and selected trace metals, but suggest that it is advantageous to diafilter the colloiddal fraction after ultrafiltration, in order to wash out the entrained low molecular weight fraction. 2) The fact that most trace metals are found in the colloiddal fraction, which is mostly made up of organic matter, suggests that current models of metal complexation in estuarine waters are, at best, incomplete, and at worst, inadequate. 3) the fact that colloiddal forms of trace metals are bioavailable to Penaeid shrimp suggests that the Free Ion Activity (FIA) model needs to be amended for aquatic organisms such as shrimp. 4) The observation that trace metals can be complexed by two different types of ligands, one which is coagulating rapidly with particles, and another group of less surface active ligands which keep trace metals in solution longer, suggests that equilibrium-based techniques such as electrochemical techniques will mostly see the solution forms of trace metals, while radiotracer techniques will mainly see the dynamics of trace metal association with both surface active and solution ligand groups. 5) The fact that we were able to repeat our initial observations of Ag complexing to macromolecular thiolic groups (phytochelatins or metallothioneins) suggests that this feature is ubiquitous. 6) The fact that radiocarbon- and polysaccharide-rich fibrils are major components of COM in Galveston Bay, Gulf of Mexico and in Middle Atlantic Bight waters, combined with their proven complexant capabilities for many A and borderline metal ions suggests that they likely play an important role in the transport of trace metals in estuarine and continental margin waters.

TRANSITIONS

In addition to the PIs, Assistant Research Scientist, Dr. Liang-Saw Wen, graduate student Degui Tang, and research assistant Susan Gonzalez have been supported on this project. The fact that many

publications resulting from this research are frequently cited in the literature suggests that the results from this research are utilized by other researchers in the field.

RELATED PROJECTS

This project benefited from other programs which investigated marine colloids.

1) DOE, -_Ocean Margins Program, “Carbon transport in the benthic boundary layer”: Investigation of the importance of benthic boundary layer processes in ocean margins for COM export to open ocean. Determination of isotopic and elemental composition of marine colloids.

2) NSF - OCE, “Relationship of Th(IV) speciation to scavenging in marine environments”: Investigation of the importance of parallel reactions for Th(IV) sorption to colloidal matter of all sizes.

This project benefited also from collaborations with Drs. J. Buffle, K. Wilkinson, and E. Balnois, Dept. of Analytical Chemistry, University of Geneva, Switzerland, for the AFM and TEM work on COM, and with Dr. John Cantois, Specells, Inc., Houston, TX, for the HPLC work with Ag-thiols.

PUBLICATIONS

- Carvalho, R.A., Benfield, M.C., and Santschi, P.H. 1998. Comparative bioaccumulation studies of colloiddally-complexed and free-ionic heavy metals in juvenile brown shrimp *penaeus aztecus* (crustacea: docapoda: penaeidae). *Limnol. Oceanogr.*, in review.
- Guo, L., and Santschi, P.H. 1997. Composition and cycling of colloids in marine environments, *Reviews of Geophysics*, 35, 17-40.
- Guo, L., and Santschi, P.H. 1997. Isotopic and elemental characterization of colloidal organic matter from the Chesapeake Bay and Galveston Bay. *Marine Chemistry*, in press.
- Guo, L., and Santschi, P.H. 1997. Measurements of dissolved organic carbon (DOC) in seawater by the high temperature combustion method. *Acta Oceanologica Sinica*, 16(2), 59-73.
- Guo, L., and Santschi, P.H. 1998. Trace metal composition of estuarine colloidal organic matter. *Environ. Sci. and Technol.*, in review.
- Guo, L., Santschi, P.H., and Bianchi, T.S. 1998. Dissolved organic matter in estuaries of the Gulf of Mexico. In: *Biogeochemistry of Guof of Mexico Estuaries*, T.S. Bianchi, J.R. Pennock, and R. Twilley, eds., John Wiley & Sons, in press.
- Santschi, P.H., Balnois, E., Wilkinson, K., Zhang, J., Buffle, J., and Guo, L. 1998. Fibrillar polysaccharides in marine macromolecular organic matter, as imaged by Atomic Force Microscopy and Transmission Electron Microscopy, *Limnology and Oceanography*, 43(5), 896-908.
- Santschi, P.H., Guo, L., Means, J.C., and Ravichandran, M. 1998. Natural organic matter binding of trace metal and trace organic contaminants in estuaries. In: *Biogeochemistry of Guof of Mexico Estuaries*, T.S. Bianchi, J.R. Pennock, and R. Twilley, eds., John Wiley & Sons, in press.
- Santschi, P.H., Lenhart, J., and Honeyman, B.D. 1997. Heterogeneous processes affecting trace contaminant distribution in estuaries: The role of natural organic matter. *Marine Chemistry*, in press.
- Stordal, M.C., Gill, G.A., Wen, L.-S., and Santschi, P.H. 1997. Dissolved and colloidal arsenic, antimony and selenium within three Texas estuaries. *Aquatic Geochemistry*, in review.
- Wen, L.-S., and Santschi, P.H. 1997. Estuarine trace metal distribution in Galveston Bay, II: Solid phase speciation and heterogeneous processes. *Geochim. Cosmochim. Acta*, in review.

- Wen, L.S., P.H. Santschi, C. Paternostro, and G. Gill. 1998. Estuarine trace metal distributions in Galveston Bay I: Colloidal forms and dissolved phase speciation, *Mar. Chem.*, in press.
- Wen, L.S., P.H. Santschi, G. Gill and C. Paternostro. 1997. Colloidal and particulate silver in river and estuarine waters of Texas, *Environ. Sci. and Technol.*, 31, 723-731.
- Wen, L.S., Santschi, P.H., and Tang, D. 1997. Interactions between radioactively labeled colloids and natural particles: Evidence for Colloidal Pumping. *Geochim. Cosmochim. Acta*, 61(14), 2867-2878.
- Wen, L.S., Shiller, A., Santschi, P.H., and Gill, G. 1998. Trace metal behavior in Gulf of Mexico estuaries. In: *Biogeochemistry of Gulf of Mexico Estuaries*, T.S. Bianchi, J.R. Pennock, and R. Twilley, eds., John Wiley & Sons, in press.

PRESENTATIONS

- Gill, G. A., L.-S. Wen, R. Lehman, D. Tang and P. Santschi (1997). Silver in Colorado Watersheds. Proc. 5th International Argentum Conference on the Transport, Fate, and Effects of Silver in the Environment. Hamilton, Ontario, Canada, September 28 to October 2, 1997. A.W. Andren and T.W. Bober, eds., pp.155-162.
- Guo, L., Santschi, P.H., Boland, G.W., and Lehman, R. 1998. Organic carbon cycling in ocean margin benthic nepheloid layers, AGU/ASLO meeting in San Diego, CA. EOS 79(1), Jan. 6, 1998, p. OS13.
- Santschi, P., D. Tang, L.-S. Wen, and G. Gill (1997). Macromolecular organic sulfur complexes of silver in estuarine environments of Galveston Bay. Proc. 5th International Argentum Conference on the Transport, Fate, and Effects of Silver in the Environment. Hamilton, Ontario, Canada, September 28 to October 1, 1997. A.W. Andren and T.W. Bober, eds., pp.41-49.
- Santschi, P.H. (1997) Colloids in oceanic environments. Composition and importance for trace element cycles. Paper presented at the 214th ACS National Meeting of the American Chemical Society, Las Vegas, NV, Sept. 7-11, 1997. Paper Env.002.
- Santschi, P.H., Balnois, E., Wilkinson, K., Zhang, J., Buffle, J., and Guo, L. 1998. Fibrillar polysaccharides in marine macromolecular organic matter, as imaged by Atomic Force Microscopy and Transmission Electron Microscopy, AGU/ASLO meeting in San Diego, CA. EOS 79(1), Jan. 6, 1998, p. OS13.
- Santschi, P.H., Guo, L., Walsh, I.D., Quigley, M., and Baskaran, M. 1998. Boundary exchange and scavenging of radionuclides in continental margin waters of the Middle Atlantic Bight: Implications for organic carbon fluxes, AGU/ASLO meeting in San Diego, CA. EOS 79(1), Jan. 6, 1998, p. OS183.
- Santschi, P.H., Wen, L.-S., Quigley, M., and Tang, D. 1998. Phase and chemical speciation studies of surface-bound trace metals in estuarine environments. Invited Paper. Proc. 8th Int. Symp. of SETAC, Bordeaux, France, April 14-18, 1998, pp. 28.
- Wen, L.-S., D. Tang, R. Lehman, G. Gill and P. Santschi (1997). Dissolved and colloidal Ag in natural waters - analytical aspects. Proc. 5th International Argentum Conference on the Transport, Fate, and Effects of Silver in the Environment. Hamilton, Ontario, Canada, September 28 to October 1, 1997. A.W. Andren and T.W. Bober, eds., pp.415-420.